TABLE VI

BOND ANGLES FOR NONHYDROGEN ATOMS FOR $[(CH_3)_2N(CH_2)_2N(CH_3)MgCH_3]_2$

Dimer at (0, 0, 0)		Dimer at (1/2, 1/2, 1/2)	
Atoms	Angle, deg	Atoms	Angle, deg
N(2)-Mg-N(1)	83.36 (13)	N(2)-Mg′-N(1)	83.97 (12)
N(2)-Mg-C(1)	115.19 (16)	N(2)′-Mg-C(1)	117.40 (17)
N(2)-Mg-N(1)′	112.02 (13)	N(2)′-MgN(1)	109.80 (14)
N(1)-Mg-C(1)	126.66 (16)	N(1)′-Mg-C(1)	130.26 (16)
N(1)-Mg-N(1)′	91.70 (12)	N(1)′-Mg-N(1)	91.38 (12)
C(1)-Mg′-N(1)	120.86 (16)	C(1)-Mg-N(1)	117.75 (17)
Mg-N(1)-Mg′	88.30 (12)	Mg-N(1)-Mg′	88.62 (12)
Mg-N(1)-C(2)	119.64 (26)	Mg-N(1)-C(2)	116.32 (25)
Mg-N(1)-C(3)	111.03 (25)	Mg-N(1)-C(3)	110.22 (24)
C(2)-N(1)-Mg′	117.89 (26)	C(2)-N(1)-Mg′	122.43 (25)
C(2)-N(1)-C(3)	108.77 (33)	C(2)-N(1)-C(3)	108.22 (25)
C(3)-N(1)-Mg′	109.79 (25)	C(3)-N(1)-Mg′	109.64 (23)
Mg-N(2)-C(5)	107.42 (25)	Mg′-N(2)-C(6)	106.23 (27)
Mg-N(2)-C(6)	119.39 (28)	Mg′-N(2)-C(5)	120.66 (24)
Mg-N(2)-C(4)	101.14 (24)	Mg-N(2)-C(4)	100.98 (23)
C(5)-N(2)-C(6)	107.74 (35)	C(5)-N(2)-C(6)	108.03 (33)
C(6)-N(2)-C(4)	111.61 (35)	C(5)-N(2)-C(4)	109.88 (33)
C(5)-N(2)-C(4)	109.43 (35)	C(6)-N(2)-C(4)	110.75 (32)
C(4)-C(3)-N(1)	111.40 (34)	C(4)-C(3)-N(1)	110.54 (32)
N(2)-C(4)-C(3)	111.95 (36)	N(2)-C(4)-C(3)	112.44 (35)

consideration of thermal motion is 2.100 (4) Å for dimer I and 2.104 (4) Å for dimer II. With the inclusion of thermal motion with the C(1) atom riding on the Mg atom, the interatomic distance is 2.126 (4) Å for dimer I and 2.117 (4) Å for dimer II.

Hydrogen atoms were included in the structure refinement. The average carbon–hydrogen bond length for dimer I is 0.98 (3) Å and, for dimer II, it is also 0.98 (3) Å. Light atom–hydrogen atom distances determined by X-ray analyses are well known to be abnormally short when compared to values obtained by spectroscopic methods and the average values reported above are not inconsistent with the often quoted spectroscopic C–H bond length of 1.1 Å.

CONTRIBUTION FROM LAWRENCE RADIATION LABORATORY AND DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA 94720

Preparation and Crystal Structures of Dicesium Berkelium Hexachloride and Dicesium Sodium Berkelium Hexachloride[1]

BY L. R. MORSS AND J. FUGER

Received November 25, 1968

Cs_2BkCl_6 and $Cs_2NaBkCl_6$ have been prepared from aqueous solution on the scale of a few micrograms using the isotope ^{249}Bk. The crystal structures of these compounds have been investigated by X-ray powder diffraction. Cs_2BkCl_6 is not isomorphous with Cs_2PuCl_6 and Cs_2CeCl_6, which exhibit trigonal symmetry, but has double the *c* axis of these compounds, with two molecules per unit cell. The hexagonal lattice parameters (95% confidence) are a = 7.450 (3) Å and c = 12.098 (5) Å. $Cs_2NaBkCl_6$ is face-centered cubic and isomorphous with the corresponding americium compound. The lattice parameter is a = 10.805 (3) Å; the crystal contains four molecules per unit cell.

Because of the comparatively short half-life and presently restricted availability of berkelium (as ^{249}Bk), the preparation and characterization of its compounds present an interesting challenge in inorganic synthesis. If these difficulties can be overcome, basic information can be obtained on the trivalent chemistry of this element and on its even more interesting tetravalent properties.

The frequently observed parallels in berkelium and cerium chemistry focused our interest on a marginally stable compound of tetravalent cerium, Cs_2CeCl_6. We had prepared this compound easily by precipitation from ice-cold concentrated HCl and with considerable difficulty by heating an intimate mixture of $CeCl_3$ and CsCl for several days in several atmospheres pressure of Cl_2. We selected the "wet" preparation as preferable, although it involved more mechanical manipulations. (The major technical difficulty was the quantitative removal of dried, centrifuged precipitate from the bottom of a capillary microcone.)

---

[1] This work was performed under the auspices of the United States Atomic Energy Commission.

Experimental Section

As a preliminary to the proposed synthesis of Cs_2BkCl_6, techniques were first developed for the microgram-scale synthesis of Cs_2CeCl_6. Beginning with a solution of 1 μg of Ce(III) in 1 μl of 2 *M* H_2SO_4, methods of oxidation and precipitation were investigated systematically; the procedure which gave the optimum yield of Cs_2CeCl_6 was subsequently applied to the experiments with Bk. In particular, the tetravalent hydroxide was selected as an appropriate intermediate because the stability against reduction, ease of precipitation, and speed of dissolution of Bk(IV) and Ce(IV) hydroxides were expected to be similar.

Sources of Berkelium.—Preliminary experiments utilized 4 μg of ^{249}Bk (which had been recovered from ion-exchange beads used for magnetic susceptibility measurements) without further purification. This material contained about 0.8 μg of the decay product ^{249}Cf. Later experiments were performed with 16 and 80 μg of ^{249}Bk freshly separated from daughter activity by an α-hydroxyisobutyric acid cation-exchange column and finally purified using a leached quartz cation-exchange "clean-up" column with high-purity reagents.[2] The resulting hydrochloric acid solutions were evaporated to dryness and taken up in 2 *M* H_2SO_4 to give a final Bk concentration of 1 μg/μl. Aliquots of Bk and appropriate reagent solutions were dispensed with a microburet of quartz capillary tubing of known internal diameter.

Preparation of Cs_2BkCl_6.—A 5-μg aliquot of Bk solution in 2 *M* H_2SO_4 was placed in a quartz microcone prepared by pulling quartz tubing to a capillary tip with a thin-walled, rounded bottom of approximately 0.2-mm internal diameter. To this solution was added 5 μl of saturated $NaBrO_3$ in 2 *M* H_2SO_4. After mixing and centrifuging, the solution was heated to 90° in a water bath for 3 min to accelerate oxidation of Bk(III) to Bk(IV). The cooled solution was then made basic by adding 5 *M* aqueous NH_4OH until precipitation was complete. About 25 μl of the NH_4OH solution was required to reduce excess bromate and neutralize the sulfuric acid. (This procedure was developed from the preliminary experiments with cerium. Hot 1 *M* BrO_3^- was required to achieve rapid oxidation; neutralization with gaseous NH_3 usually resulted in considerable precipitation of NH_4BrO_3.)

The resulting precipitate was centrifuged and washed three times with water. The precipitate, presumably $Bk(OH)_4$, was yellow-green and similar in physical appearance to $Ce(OH)_4$.

After centrifuging for 1 hr, excess water was removed by pipetting and the cone was cooled to the melting point of CCl_4 (−23°), freezing the hydroxide precipitate. A freshly prepared solution of 0.1 *M* CsCl in concentrated HCl containing dissolved Cl_2 was pipetted into the reaction cone to provide about 20 mol % excess of Cs over that required for Cs_2BkCl_6. In rapid sequence, HCl gas was blown into the cone to replace most of the air and to maintain the solution saturated in HCl, the cone was covered with Parafilm and centrifuged briefly (in order to force all reagents into the capillary tip) in a chilled centrifuge tube, and the reagents were stirred to ensure complete dissolution of $Bk(OH)_4$.

It was possible to observe the stirring operation under the microscope. The hydroxide dissolved to give a red solution, from which a red-orange precipitate formed immediately. The cone was recentrifuged and the supernatant solution was removed. The precipitate was then washed once with glacial acetic acid (to remove water) and three times with diethyl ether. After the final washing, the orange precipitate dried rapidly as the ether evaporated; the reaction cone was immediately capped and mounted *in toto* as an X-ray capillary. γ radioactivity monitoring showed that about half of the Bk remained with the washed precipitate.

Preparation of $Cs_2NaBkCl_6$.—The first two preparations of Cs_2BkCl_6 had been carried out with 1-μg portions of Cf-contaminated berkelium. In order to prove that the orange precipitate would not form under nonoxidizing conditions and therefore that it was a compound of Bk(IV), 1 μg of Bk solution was carried through steps identical with those described above in a reaction microcone with a somewhat smaller capillary tip, except that sodium sulfate was substituted for sodium bromate. In this way, oxidation of Bk(III) was eliminated without altering other conditions. A *white* hydroxide precipitate was observed. Upon dissolving this precipitate in CsCl–HCl solution, no precipitate formed. However, upon blowing HCl gas over the surface of the solution and cooling the cone, a yellow crystalline precipitate appeared, first at the surface and then throughout the solution. This precipitate, very small in amount, survived washings as described above. Its X-ray powder pattern was remarkably similar to that reported for $Cs_2NaAmCl_6$, prepared recently by Bagnall, *et al.*[3] We believe that under our experimental conditions sufficient sodium for a small yield of $Cs_2NaBkCl_6$ remained from the Na_2SO_4 solution. Similar experiments have shown very imperfect washing of microscale precipitates.

Encouraged by these results, we prepared $Cs_2NaBkCl_6$ twice, using 1-μg aliquots of recently purified Bk solution in capillary-tip microcones of 0.1-mm internal diameter. For the first preparation, berkelium(III) hydroxide was precipitated with NaOH and the precipitate was washed three times with water. A solution of 0.1 *M* CsCl–0.05 *M* NaCl in 6 *M* HCl was added in about 20% excess, the hydroxide was stirred until it dissolved, and HCl gas was then blown over the solution. In this first preparation, the hydroxide was faintly green but more flocculent than the berkelium(IV) hydroxide. When HCl gas was blown into the microcone, a distinctly yellow precipitate formed, which was washed as above. Its X-ray powder pattern was again similar to that of face-centered-cubic $Cs_2NaAmCl_6$.

The subsequent preparation was performed under reducing conditions by adding hydroxylamine to the Bk solution before precipitating the hydroxide. In this preparation both the hydroxide and the final precipitate were *white*. The powder pattern of the resulting substance was face-centered cubic, identical with that of the earlier (yellow) product. (An interpretation of these observations is offered in the Discussion.)

X-Ray Diffraction Equipment.—X-Ray powder patterns were taken on Ilford G Industrial X-ray film in a 57.3-mm diameter Debye–Scherrer Philips camera with Straumanis mounting. (The camera chuck and cover were modified to accept the long capillary cones.) Copper radiation ($\lambda(K\alpha_1)$ 1.54051 Å), filtered through 0.01-mm nickel foil placed between sample and film, was generated by a Jarrell-Ash 80-000 Microfocus X-ray unit. Exposure times were 2–8 hr. Most reflections for $160° < 2\theta$ and $2\theta < 20°$ were masked by the Ni filter support. Line positions were measured visually to ±0.05 mm. Individual preparations were photographed twice and most films were read twice by independent observers on different readers. Line intensities were measured with a Jarrell-Ash microphotometer.

Analyses.—Five samples of Cs_2BkCl_6 were weighed and assayed for ^{249}Bk and ^{249}Cf by growth of α activity[4] in measured aliquots, taking the ^{249}Bk half-life as 314 days and that of ^{249}Cf as 345 years.[5] Three samples (weighing from 8 to 16 μg) were analyzed by potentiometric ultramicrotitration for Bk^{4+} with standard Fe^{2+} solution and subsequently for Cl^- with standard Ag^+. *Anal.* Calcd for Cs_2BkCl_6: Bk, 34.2; Cl, 29.24. Found: total Bk, 31.6 ± 3.5; Bk(IV), 29.9 ± 0.9; Cl, 27.8 ± 1.5. Error limits represent 95% confidence intervals and for total Bk include half-life uncertainties. The low Bk and Cl analyses, and the Cl:Bk atom ratio of 6.2:1, indicate the presence of about 7 wt % of CsCl. The most troublesome sources of potential errors were transfer losses, chloride contamination, and dust particles.

Results

Preliminary syntheses using 1-μg quantities of cerium under conditions similar to those planned for berkelium

---

[2] G. H. Higgins, Report UCRL-6134, Lawrence Radiation Laboratory, University of California, Berkeley, Calif., 1960.

[3] K. W. Bagnall, J. B. Laidler, and M. A. A. Stewart, *J. Chem. Soc., A*, 133 (1968).

[4] J. R. Peterson, Report UCRL-17875, Lawrence Radiation Laboratory, University of California, Berkeley, Calif., 1967.

[5] J. Milsted, E. P. Horwitz, A. M. Friedman, and D. N. Metta, *J. Inorg. Nucl. Chem.*, in press.

gave powder patterns of Cs_2CeCl_6 whose lattice parameters were in close agreement with those earlier reported for macroscale preparations, even when one-fifth as much lanthanum as cerium was intentionally added as a trivalent impurity. Results of the Ce experiments are shown in Table I.[6,7]

TABLE I

LATTICE PARAMETERS OF TRIGONAL Cs_2CeCl_6

Ref	a, Å	c, Å
Plumier[6]	7.484(5)	6.034(8)
Kaatz and Marcovich[7]	7.476(2)	6.039(2)
This work, 1 μg	7.480(6)	6.046(6)
This work, 1 μg with 20% La^{3+}	7.481(6)	6.040(8)

Six successful preparations of Cs_2BkCl_6 were achieved, two starting with 1 μg of Bk (contaminated with 20% Cf daughter), two using 5 μg of recently purified Bk, and two using 40 μg of recently purified Bk. (An attempted preparation using NaOH as precipitant for the hydroxide instead of NH_4OH (to avoid reduction of bromate by NH_3) resulted in a mixture of mostly $Cs_2NaBkCl_6$ with only a small amount of Cs_2BkCl_6.)

Least-squares fitting of lattice parameters to observed line positions was carried out using program LCR-2.[8] Theoretical line intensities were calculated by program POWD.[9]

All known compounds of the composition Cs_2MCl_6 exhibit either trigonal or cubic crystal structures. For the known actinide(IV) complexes of thorium through plutonium,[10] and for cerium,[7] the complexes are trigonal. Lead, zirconium, and smaller tetravalent cations form cubic complexes. Since the Bk^{4+} ion is believed to be only slightly smaller than Pu^{4+} but considerably larger than Pb^{4+}, it was anticipated that Cs_2BkCl_6 would be isostructural with the trigonal actinide(IV) hexachloro complexes. However, the powder patterns of Cs_2BkCl_6 showed that this compound is isostructural neither with Cs_2PuCl_6 nor with Cs_2PbCl_6. The powder patterns were indexable only in a hexagonal system typified by Rb_2MnF_6.[11] (It should be pointed out that some hexa*fluoro* complex compounds are polymorphic, exhibiting two or even all three of these structures.[12])

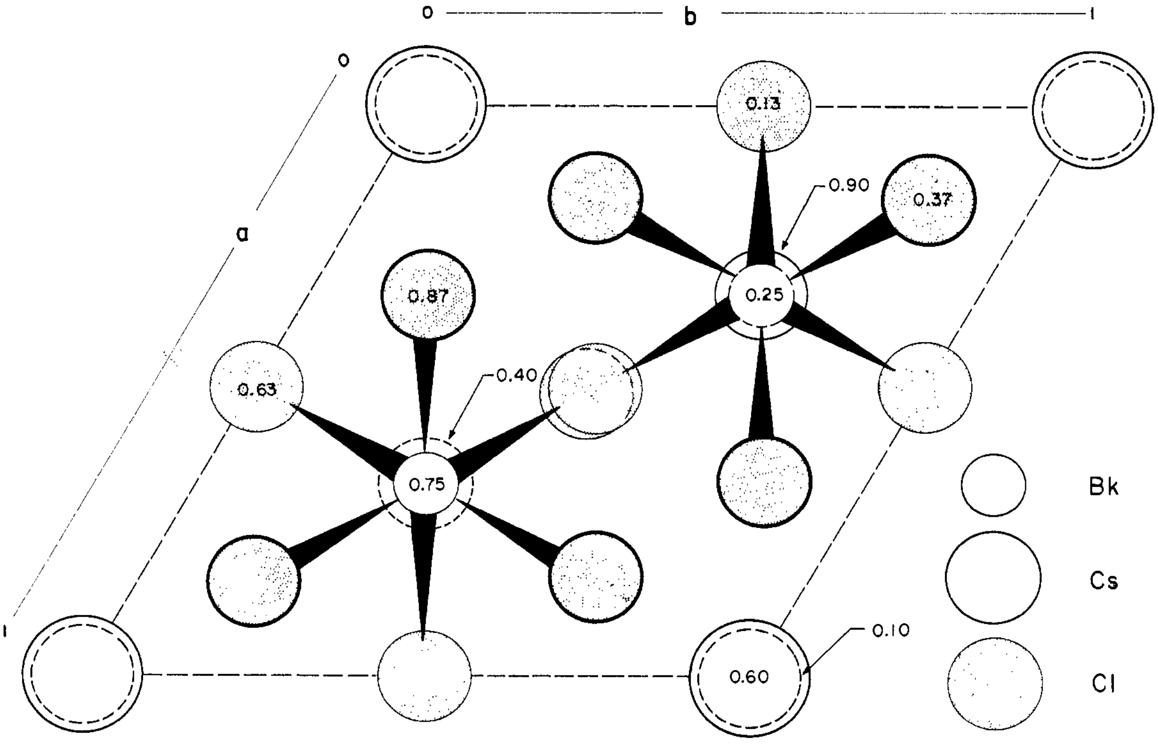

Figure 1.—Projection of a unit cell of Cs_2BkCl_6 upon the *ab* plane.

The reflection condition, namely, *hhl* ($l = 2n$), and special atomic positions are appropriate for space groups P31c, P$\bar{3}$1c, $P6_3mc$, P$\bar{6}$2c, and $P6_3/mmc$. The most reasonable space group is $P6_3mc$ (C_{6v}^4), since this space group is the only one which permits approximately octahedral coordination of Cl^- ions about Bk^{4+} ions and which also allows Cs^+ ions to maintain 12-fold coordination. Atomic positions are as follows: 2 Bk (b) at $^1/_3$, $^2/_3$, z; 2 Cs (b) at $^1/_3$, $^2/_3$, $z + 0.645$; 2 Cs (a) at 0, 0, $z - 0.145$; 6 Cl (c) at 0.17, −0.17, $z + 0.12$; 6 Cl (c) at 0.495, −0.495, $z - 0.12$. Atomic positions not fixed by the space group were estimated by comparison with those of Rb_2MnF_6 and by ionic radius sums; therefore, no error limits are given. Figure 1 is a projection of the unit cell upon the *ab* plane, with z set (arbitrarily) at 0.25.

Unit cell dimensions were calculated by averaging 2θ

---

[6] C. Plumier, Thesis, Laboratory of Nuclear Chemistry, University of Liege, Liege, Belgium, 1966.

[7] T. Kaatz and M. Marcovich, *Acta Cryst.*, **21**, 1011 (1966).

[8] D. E. Williams, Ames Laboratory Report IS-1052 (1964).

[9] D. K. Smith, Report UCRL-7196, Lawrence Radiation Laboratory, University of California, Livermore, Calif., 1963.

[10] W. H. Zachariasen, *Acta Cryst.*, **1**, 268 (1948).

[11] H. Bode and W. Wendt, *Z. Anorg. Allgem. Chem.*, **269**, 165 (1952).

[12] A. F. Wells, "Structural Inorganic Chemistry," Oxford University Press, London, 1962, p 368.

Table II

Powder Pattern Line List for Cs_2BkCl_6 (Hexagonal)

No. Obs.	I_{obs}	d_{obs}	h	k	l	d_{calc}	I_{calc}[a]
1	60[b]	5.93	0	0	2	6.05	20
1	52[b]	5.74	1	0	1	5.69	97
6	40[b]	4.411	1	0	2	4.413	61
6	100[b]	$3.712\alpha_1$ $3.732\alpha_2$	1	1	0	3.726	100
6	40[b]	3.422	1	0	3	3.420	75
6	32	3.173	1	1	2	3.172	22
4	5[b]	3.116	2	0	1	3.117	21
5	5[b]	3.018	0	0	4	3.024	5
6	55	2.846	2	0	2	2.847	83
5	22	2.735	1	0	4	2.738	18
6	46	2.519	2	0	3	2.519	62
3	2[b]	2.430	2	1	0	2.439	2
6	18	2.392	2	1	1	2.391	20
6	52	2.260	1 2	0 1	5 2	2.265 2.262	36
6	27	2.202	2	0	4	2.206	16
6	37	2.150	3	0	0	2.151	13
6	47	2.087	2	1	3	2.087	43
6	23	2.025	3	0	2	2.027	7
6	60	1.934	2	0	5	1.936	22
5	37	1.895	2	1	4	1.898	13
6	70	1.861	2	2	0	1.863	41
6	58	1.774	1 3	1 1	6 1	1.773 1.771	36
6	70	1.714	2 3 2	1 1 0	5 2 6	1.718 1.716 1.710	35
6	7	1.668	1	0	7	1.669	2
6	24	1.636	3	1	3	1.636	19
2	4	1.600	4	0	1	1.599	3
5	6	1.588	2	2	4	1.586	3
6	20	1.557	4 2	0 1	2 6	1.559 1.554	14
2	6	1.540	3	1	4	1.540	7
4	20	1.512	0	0	8	1.512	5
4	20	1.4966	4	0	3	1.4978	12
6	24	1.4704	1 3 3	0 0 2	8 6 1	1.4722 1.4710 1.4694	24
6	25	1.4375	3 3	1 2	5 2	1.4388 1.4379	13
2	39	1.4105	2 4	1 1	7 0	1.4100 1.4081	15
6	24[b]	1.4042	1	1	8	1.4011	7
3	10[b]	1.3890	3	2	3	1.3897	11
6	26	1.3694	4 2 2	1 0 2	2 8 6	1.3714 1.3692 1.3682	14
5	17	1.3419	4 3	0 1	5 6	1.3422 1.3384	8
2	2[b]	1.3287	3	2	4	1.3296	4
6	15[b]	1.2616	3 5 4	2 0 0	5 2 6	1.2627 1.2621 1.2596	10
6	16[b]	1.2393	3 3 2 3	1 3 0 0	7 0 9 8	1.2432 1.2418 1.2408 1.2370	13
3	8[b]	1.2144	3 4	3 2	2 1	1.2165 1.2133	4
5	6[b]	1.1948	4 3	2 2	2 6	1.1954 1.1932	11
3	6[b]	1.1892	1 5	0 0	10 4	1.1890 1.1870	3
6	12[b]	1.1758	2 2	1 2	9 8	1.1772 1.1740	16
3	8[b]	1.1687	4	2	3	1.1672	11
5	12[b]	1.1538	3 4 5	1 1 1	8 6 1	1.1550 1.1544 1.1537	19
3	5[b]	1.1316	2 4	0 2	10 4	1.1327 1.1310	6
2	5[b]	1.0901	4	2	5	1.0890	7
4	15[b]	1.0869	5	0	6	1.0869	0.4
2	6[b]	1.0842	1 2	0 1	11 10	1.0841 1.0837	5
5	12[b]	1.0757	6 3	0 1	0 9	1.0755 1.0748	13
5	12[b]	1.0570	6 3 3 4	0 2 3 3	2 8 6 1	1.0588 1.0578 1.0574 1.0568	11
6	12[b]	1.0433	5 4 4	1 3 2	5 2 6	1.0452 1.0449 1.0434	10
6	16[b]	1.0306	5 4 4	2 0 1	0 9 8	1.0333 1.0326 1.0305	13
4	12[b]	1.0012	2 3 4	1 1 3	11 10 4	1.0025 1.0022 1.0010	10
3	8[b]	0.9958	4 1 3	2 0 2	7 12 9	0.9964 0.9960 0.9951	7
2	6[b]	0.9695	4	0	10	0.9678	2
3	2[b]	0.9595	3	3	8	0.9597	3
4	10[b]	0.9369	3 3 6	1 2 1	11 10 4	0.9370 0.9367 0.9358	9
5	10[b]	0.9312	2 4 5	1 4 0	12 0 9	0.9316 0.9314 0.9309	12
5	12[b]	0.9198	4 5 5 7 5	4 1 2 0 3	2 8 6 1 1	0.9205 0.9198 0.9195 0.9192 0.9192	17
2	4[b]	0.9123	3 6 7 5	0 1 0 3	12 5 2 2	0.9128 0.9115 0.9113 0.9113	9
3	6[b]	0.9092	4	0	11	0.9087	3
2	2[b]	0.8984	7 5	0 3	3 3	0.8986 0.8986	7
2	4[b]	0.8936	2 6	0 2	13 1	0.8941 0.8924	3
2	< 2[b]	0.8830	3	2	11	0.88[illegible]	5
3	6[b]	0.8752	6 6	0 2	8 3	0.8764 0.8736	20
5	12[b]	0.8539	6 4 7 5	1 0 1 2	7 12 0 8	0.8551 0.8549 0.8547 0.8531	17
2	8[b]	0.8390	6	2	5	0.8393	8
2	2[b]	$0.8242\alpha_1$	6 5	1 4	8 1	0.8248 0.8243	7
2	4[b]	$0.8168\alpha_1$	4	2	11	0.8167	10
1	< 2[b]	$0.8127\alpha_1$	6	3	0	0.8130	9
1	< 2[b]	$0.8064\alpha_1$	4	0	13	0.8060	3
2	2[b]	$0.7976\alpha_1$	5 4 5	1 3 4	11 10 4	0.7977 0.7976 0.7970	19
1	6[b]	$0.7928\alpha_1$ $0.7928\alpha_2$	4	4	8	0.7930	20
1	4[b]	$0.7909\alpha_1$	8	0	3	0.7909	10

Notes: (a) Scaled from POWD Program to $I_{110} = 100$. Entries refer to h k l values in center column and are for overall $(\alpha_1+\alpha_2)$ intensities.

(b) Estimated visually because film saturation on high background precluded accurate densitometer reading.

values (after correction for film shrinkage) from six films representing all six preparations. Program LCR-2 weights each line proportional to $1/[(\sin^2 (2\theta))\sigma^2(\theta)]$, where $\sigma(\theta)$ is the average error of a single line reading from the mean (of readings of that line on all films). In many cases observed lines were considered to be superpositions of two or more theoretically possible lines. In these situations each of the theoretically possible lines was assigned to the observed 2θ value and weighted with respect to its calculated intensity such that the over-all weight of the group remained $1/[(\sin^2 (2\theta))\sigma^2(\theta)]$, $\sigma(\theta)$ still being the average error of the observed line reading from the mean. This was accomplished by normalizing all calculated intensities for a group of superposed lines to $\Sigma I = 1$, and setting $\sigma_i = \sigma_{net}/(I_i)^{1/2}$. Lattice parameters so calculated are $a = 7.451$ (1) Å and $c = 12.097$ (2) Å. Error limits are standard deviations representing only internal consistency of averaged values of observed 2θ.

As an alternative (and chemically more meaningful) method of calculating lattice parameters, 2θ values from *each* film were used to calculate lattice parameters for that film. The mean values, with error limits representing 95% confidence limits for the six preparations (by applying the Student t value of 2.6 to standard deviations generated from the six sets of lattice parameters), are $a = 7.450$ (3) Å and $c = 12.098$ (5) Å. Use of the powder pattern extrapolation function appropriate for sample thickness and self-absorption increased lattice parameters by less than 0.001 Å because of the small sample size.

For this crystal structure, the formula weight is 727.60, the cell volume is 581.5 Å^3, and the calculated density is 4.155 g/cm^3. There are two formula units per unit cell.

Table II is a list of powder lines for averaged values from the six films. Table III is a similar list for unindexed lines; those attributable to known impurities are so indicated. A measure of the rate of decomposition of Cs_2BkCl_6 due to radioactivity and atmospheric moisture is the "growth" of unindexed lines: one 5-μg sample with 61 indexable lines showed one unindexable line of trace intensity 4 hr after preparation, seven impurity lines after 18 hr, and ten impurity lines after 96 hr (during 18 of which the sample had been exposed to an X-ray beam), including two lines of medium intensity.

TABLE III

POWDER PATTERN IMPURITIES IN Cs_2BkCl_6

d, Å	Intens[a]	No. obsd	Identification
4.240	8	1	
3.870	10	2	$Cs_2NaBkCl_6$ 220
3.317	4	1	
3.052	4	1	
2.919	8	2	CsCl 100
2.639	8	4	
2.328	2	2	
1.519	4	1	
1.506	4	1	

[a] Estimated visually; scale is the same as for Table II.

$Cs_2NaBkCl_6$ is face-centered cubic, as are $Cs_2NaAmCl_6$[3] and many other compounds A_3BX_6 and A_2BCX_6.[13] The "ideal cryolite" structure which has been determined for some of these compounds has space group Fm3m (O_h^5). Comparison of observed and calculated intensities for $Cs_2NaBkCl_6$ indicates that this structure is appropriate, with atomic positions as follows: 4 Bk (a) at 0, 0, 0; 4 Na (b) at $^1/_2$, $^1/_2$, $^1/_2$; 8 Cs (c) at $^1/_4$, $^1/_4$, $^1/_4$; 24 Cl (e) at x, 0, 0. (All atomic positions are repeated by the face-centering operation.) The Cl x parameter was determined to be 0.24 (1) Å by minimizing the difference between observed and calculated intensities.

The lattice parameter, a, calculated (by both methods described above) from four films obtained from two preparations, is 10.805 (3) Å (95% confidence). The formula weight is 750.59, the cell volume is 1261.5 Å^3, the calculated density is 3.952 g/cm^3, and there are 4 formula units per unit cell. Table IV is a list of averaged d spacings from the four films. All lines are included for calculated intensities greater than 1. Table V lists the powder pattern impurities in $Cs_2NaBkCl_6$. The stability of $Cs_2NaBkCl_6$ when stored in air is indicated by an essentially unchanged lattice parameter of 10.810 Å and the presence of only two impurity lines in the powder pattern of a 3 month old sample.

Since the lattice parameters of Cs_2CeCl_6 did not change significantly when La^{3+} was present in the Ce^{4+} reagent (Table I), it was expected that trivalent impurities would not coprecipitate with Cs_2BkCl_6. Most of the assayed samples were taken from a single synthesis; the Bk reagent used in this synthesis contained 3.3% ^{249}Cf (due to ^{249}Bk decay during the 15 days since the Bk–Cf column separation). The α assays showed 0.1% Cf in the Cs_2BkCl_6 (extrapolated back to the date of synthesis). The failure of Cf(III) to coprecipitate represents further evidence of the preparation of a Bk(IV) compound. It is to be expected that Cf will coprecipitate with $Cs_2NaBkCl_6$. On this assumption the average Cf:Bk ratio in $Cs_2NaBkCl_6$ samples when X-rayed was 0.018. Table VI gives interatomic distances in both compounds.

Discussion

The berkelium hydroxide precipitated after bromate oxidation invariably was green (actually yellowish green). We believe this species to be $Bk(OH)_4$ or, more properly, a hydrous oxide of Bk(IV). The intense orange color of Cs_2BkCl_6 is probably caused by a strong Bk^{4+}–Cl electron-transfer band.

The experiment performed with Bk(III) under reducing conditions (using hydroxylamine) indicated that both $Bk(OH)_3$ and $Cs_2NaBkCl_6$ are white. However, we observed a green hydroxide and a yellow $Cs_2NaBkCl_6$ when neither oxidizing nor reducing reagents were added to the original solution. We conclude that $Bk(OH)_3$, like $Ce(OH)_3$, is slowly oxidized to berkelium(IV) hydroxide by air and/or solution radiolysis products. The yellow color of $Cs_2NaBkCl_6$ precipitated from this hydroxide is most likely due to a small amount of the intensely colored tetravalent chloro complex $BkCl_6^{2-}$.

The ease of precipitation of Cs_2BkCl_6 from chloride solution demonstrates the thermodynamic stability of aqueous Bk(IV) chloro complexes, since Bk(IV) (uncomplexed) is a stronger oxidant than Cl_2 by about 0.26 V.[14,15] We believe that Bk(IV) chloro complex ions are at least as thermodynamically stable (toward dissociation or reduction) as corresponding Ce(IV) ions in aqueous HCl, because Cs_2BkCl_6 can be prepared easily from aqueous HCl despite the presence of chloride and radiolytically produced reducing agents.

Some qualitative conclusions may be inferred from observations made during the preparation of these chloro complexes. It is possible to precipitate $Cs_2NaBkCl_6$ from HCl solution at room temperature. Similar precipitation of $Cs_2NaAmCl_6$ in this laboratory required high HCl concentration and cooling; furthermore, no such compound of plutonium could be precipitated even from saturated HCl at 0° or by evaporating to dryness. It appears, therefore, that the solubility of these compounds decreases with decreasing ionic radius,

---

(13) See ref 12, p 369.

(14) B. B. Cunningham, *J. Chem. Educ.*, **36**, 32 (1959).

(15) C. Musikas and R. Berger in "Lanthanide–Actinide Chemistry," Advances in Chemistry Series, No. 71, American Chemical Society, Washington, D. C., pp 296–307.

Table IV

Powder Pattern Line List for $Cs_2NaBkCl_6$ (Cubic)

I_{obs}	d_{obs}	h	k	l	d_{calc}	I_{calc}[a]
32[b]	6.20	1	1	1	6.238	85
9[b]	5.38	2	0	0	5.403	6.3
100[b]	3.822α 3.818β	2	2	0	3.820	156
34	3.268	3	1	1	3.258	48
16	3.114	2	2	2	3.119	15
68[b]	2.699α 2.702β	4	0	0	2.701	88
20	2.478	3	3	1	2.479	19
3	2.417	4	2	0	2.416	3.6
55[b]	2.204	4	2	2	2.206	71
21	2.080	5 3	1 3	1 3	2.079	22
47	1.910	4	4	0	1.910	56
23	1.826	5	3	1	1.826	22
---	-----	6 4	0 4	0 2	1.801	2.0
30	1.709	6	2	0	1.708	32
10	1.649	5	3	3	1.648	6.9
4	1.628	6	2	2	1.629	2.9
21	1.558	4	4	4	1.560	18
14	1.512	7 5	1 5	1 1	1.513	17
---	-----	6	4	0	1.498	1.0
34	1.443	6	4	2	1.444	35
17	1.406	7 5	3 5	1 3	1.407	11.5
10	1.3494	8	0	0	1.3506	7.8
5	1.3204	7	3	3	1.3200	2.1
17	1.2725	8 6	2 6	2 0	1.2734	16
10	1.2472	7 5	5 5	1 5	1.2477	7.2
17	1.2072	8	4	0	1.2080	21
4	1.1843	7 9	5 1	3 1	1.1860	7.8
8	1.1520	6	6	4	1.1518	8.1
5	1.1312	9	3	1	1.1327	5.5
15	1.1025	8	4	4	1.1028	16
7	1.0846	7 9 7	7 3 5	1 3 5	1.0860	5.8
20	1.0590	10 8	2 6	0 2	1.0595	19
10	1.0443	9 7	5 7	1 3	1.0446	6.9
6	1.0056	9	5	3	1.0076	5.0
12	0.9863	10	4	2	0.9864	11.4
2	0.9739	11 7	1 7	1 5	0.9743	2.7
6	0.9545α_1	8	8	0	0.9550	6.0
9	0.9438α_1	11 9 9	3 7 5	1 1 5	0.9440	9.3
10	0.9265α_1	10 8	6 6	0 6	0.9265	11.0
6	0.9169α_1	11 9	3 7	3 3	0.9165	4.5
14	0.9002α_1	12 8	0 8	0 4	0.9004	15
1[b]	0.8913α_1	11 7	5 7	1 7	0.8912	3.7
13	0.8765α_1 0.8764α_2	10 12	6 2	4 2	0.8764	17
5[b]	0.8680α_1	9 11	7 5	5 3	0.8679	8.1
12[b]	0.8547α_1 0.8546α_2	12	4	0	0.8542	13.3
1[b]	0.8465α_2	9	9	1	0.8463	3.7
	0.8444α_1	12 10 8	4 8 8	2 0 6	0.8437	2.7
5[b]	0.8336α_1 0.8341α_2	10	8	2	0.8336	13.1
7[b]	0.8263α_1 0.8256α_2	11 11 9 13	7 5 9 1	1 5 3 1	0.8263	13.1
5[b]	0.8145α_1 0.8143α_2	12	4	4	0.8145	16.7
7[b]	0.8078α_1 0.8074α_2	11 13 9	7 3 7	3 1 7	0.8076	13.8
5[b]	0.8054α_1	12 10	6 8	0 4	0.8054	3.5
12[b]	0.7967α_1 0.7964α_2	12	6	2	0.7966	17.6
2[b]	0.7904α_1 0.7902α_2	13 9	3 9	3 5	0.7902	12.5

Notes: (a) Scaled from POWD program to mean of observed intensities (I_{220} = 100). Entries refer to h k l values in center column and are for overall ($\alpha_1 + \alpha_2$) intensities.

(b) Estimated visually because film saturation or high background precluded accurate densitometer reading.

Table V

Powder Pattern Impurities in $Cs_2NaBkCl_6$

d, Å	Intens[a]	No. obsd	Identification
2.824	4	2	NaCl 200
2.356	<2	1	
1.993	<2	1	NaCl 220
1.864	<2	2	

[a] Estimated visually; scale is the same as in Table IV.

Table VI

Interatomic Distances (Å)

	Cs_2BkCl_6	$Cs_2NaBkCl_6$
Bk–Cl	6 at 2.55[a]	6 at 2.58 (10)
Na–Cl	. . .	6 at 2.82 (12)
Bk–Bk	6 at 7.42[b] 6 at 7.45[b]	12 at 7.64[b]
Cs(a)–Cl	6 at 3.74[a] 3 at 3.88[a] 3 at 3.59[a]	12 at 3.82 (1)
Cs(b)–Cl	6 at 3.74[a] 3 at 3.90[a] 3 at 3.53[a]	

[a] No error limits given because atomic positions are estimates. [b] Fixed by symmetry.

as has been observed for the Cs_2MCl_6 compounds by Bagnall, *et al.*[16,17]

It is worthwhile to compare the structures of Cs_2PuCl_6 and Cs_2BkCl_6. The former has "layers" (perpendicular to the *c* axis) with each layer consisting of $PuCl_6^{2-}$ groups with Cs^+ approximately in the planes of lower and upper chlorides. Cs_2BkCl_6 doubles the *c* axis, with alternate layers rotated 180° about sixfold screw axes. As pointed out by Wells,[18] such compounds are examples of close-packed arrays of the general com-

---

(16) K. W. Bagnall, A. M. Deane, T. L. Markin, P. S. Robinson, and M. A. A. Stewart, *J. Chem. Soc.*, 1611 (1961).

(17) For a self-consistent table of ionic radii, see J. R. Peterson and B. B. Cunningham, *Inorg. Nucl. Chem. Letters*, **3**, 327 (1967). On the same basis the ionic radius of Ce^{4+} is 0.903 Å.

(18) See ref 12, p 374 ff.

position $A_xM_yX_{3x}$, where A and X are ions of similar size. In the case Cs_2MCl_6, layers of $Cs^+ + 3\ Cl^-$ ions form close-packed "planes" and M^{4+} ions fill alternate octahedral holes formed by six Cl^- ions. In Cs_2PbCl_6 the "planes" are in cubic close packing, ABCABCABC. Cs_2PuCl_6 corresponds to hexagonal close packing, ABABAB, while Cs_2BkCl_6 is double-hexagonal close packed, ABACABAC. A crystal of ideally hexagonally packed spheres has $c/a = 1.633$. Compounds A_2MX_6 having double-hexagonal close-packed layers have c/a near this value, rather than double it, because all atoms are not identical and the unit cell base has a length double that of hexagonally closest packed metals. Thus c/a for Cs_2BkCl_6 (1.624) is double that of Cs_2PuCl_6 (0.812). Compounds Cs_2NaMCl_6 have the cubic close-packed arrangement of $Cs^+ + 3\ Cl^-$ layers, with Na^+ and M^{3+} each filling half of the octahedral holes.

Acknowledgments.—We thank Professor B. B. Cunningham for his advice and support. J. F. wishes to acknowledge the financial support of the Fonds National de la Recherche Scientifique, Brussels, Belgium, which made his stay at the Lawrence Radiation Laboratory possible.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
BRIGHAM YOUNG UNIVERSITY, PROVO, UTAH 84601

High-Pressure Synthesis of Rare Earth Diantimonides[1]

BY NORMAN L. EATOUGH[2] AND H. TRACY HALL

Received December 12, 1968

New rare earth diantimonides of orthorhombic ($LaSb_2$ type) crystal structures were prepared for Pr, Gd, and Tb. Also, new diantimonides of Gd, Tb, Dy, Ho, Er, Tm, Yb, and Y indexed as orthorhombic with two molecules per unit cell were made. Pressures to 70 kbars with simultaneous temperatures to 1800° were employed in the work.

Introduction

In a series of rare earth compounds R_iB_j where the rare element R is varied, it is common to find that the compounds have been prepared for only a certain range of R. For example, rare earth diantimonides, RSb_2, have previously been known only for the lighter rare earths. Efforts to synethesize diantimonides for Gd and heavier rare earths by ordinary techniques have not been successful (except for Yb, which often displays exceptional behavior).[3] In this and similar situations it has been reasoned that size differences between atoms R and B, due to the lanthanide contraction, lead to instability of the crystal structures thus limiting the range of R.

High pressure is capable of altering the relative sizes of atoms and has been used in the present work, simultaneously with high temperature, to provide a favorable thermodynamic and kinetic situation for the synthesis of diantimonides of the heavier rare earth elements. Once formed, the compounds remain stable (or metastable) on return to normal room conditions.

Previous Work

Earlier studies of rare earth–antimony systems include those of Vogel and Klose,[4] who in 1954 reported the compounds La_2Sb, La_3Sb_2, LaSb, and $LaSb_2$. The latter compound, $LaSb_2$, was the first rare earth diantimonide discovered. In 1966, Olcese[5] reported the formation of Ce_2Sb, Ce_3Sb_2, CeSb, and $CeSb_2$. Bodnar and Steinfink in 1967 reported the discovery of the ytterbium compounds $YbSb_2$, YbSb, Yb_5Sb_4, Yb_4Sb_3, Yb_5Sb_3, and Yb_5Sb_2.[6] The first specific study on the diantimonides was reported by Wang and Steinfink in 1967.[3] They prepared $LaSb_2$, $CeSb_2$, $NdSb_2$, $SmSb_2$, and $YbSb_2$. They attempted the synthesis of the diantimonides of Gd, Dy, Ho, and Er but were not able to make them. They did not work with Pr, Eu, Tb, Tm, or Lu. By single-crystal X-ray diffraction techniques the diantimonides of La, Ce, Nd, and Sm were found to have an orthorhombic structure which Wang and Steinfink designated as the $LaSb_2$-type structure. $YbSb_2$ was shown to have a $ZrSi_2$-type structure. They found the Sb–Sb bond distance to be very short in the $LaSb_2$-type structure and postulated that as the rare earth size decreases the Sb–Sb repulsion from increasingly shorter Sb–Sb bonds causes the structure to become unstable at Gd. A summary of the known rare earth–antimony compounds is given in Table I.

Experimental Section

Our high-pressure, high-temperature studies of the rare earth diantimonides were carried out in a tetrahedral anvil apparatus equipped with anvil guide.[7,8] The triangular faces of the tungsten carbide were 19 mm on an edge.

The rare earth metals were obtained from Research Chemicals,

---

[1] This research supported by the National Science Foundation and the Army Research Office, Durham, N. C.

[2] Now at California State Polytechnic College, San Luis Obispo, Calif.

[3] R. Wang and H. Steinfink, *Inorg. Chem.*, **6**, 1685 (1967).

[4] R. Vogel and K. Klose, *Z. Metallk.*, **45**, 633 (1954); *Chem. Abstr.*, **49**, 2844 (1955).

[5] G. L. Olcese, *Atti Accad. Nazl. Lincei, Rend., Classe Sci. Fis., Mat. Nat.*, **40**, 629 (1966); *Chem. Abstr.*, **65**, 17877 (1966).

[6] R. E. Bodnar and H. Steinfink, *Inorg. Chem.*, **6**, 327 (1967).

[7] H. T. Hall, *Rev. Sci. Instr.*, **29**, 267 (1958).

[8] H. T. Hall, *ibid.*, **33**, 1278 (1962).